

Micro-Machined Thin Film H₂ Gas Sensors

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Objectives

- Optimize process conditions, focusing on improving yield and uniformity.
- Investigate the physics and chemistry of the sensing materials and sensing mechanisms.
- Develop improved sensor packaging and electronics system integration.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- B. Sensors

Approach

- Introduce new process steps to improve device yield.
- Analyze chemical, electrical, and mechanical aspects of sensor characteristics.
- Survey device packaging possibilities; down-select most appropriate option.
- Develop real-time signal conditioning and processing algorithms and platforms.
- Implement industry-standard control practices and knowledge-based management (KBM).

Accomplishments

- Improved the post-packaging fabrication yield to greater than 80%.
- Created novel surface treatment methodology for surface micro-machined structures.
- Identified novel piezo-resistive transduction mechanisms.
- Designed a microprocessor-based evaluation kit equipped with on-board signal conditioning and processing.

Future Directions

- Evaluate characteristics of sensors fabricated with new processing steps.
- Explore new piezo-resistive device structures.
- Tailor sensors for specific applications.
- Deploy evaluation kits to test sites.

Introduction

There is a common need in all hydrogen applications to detect and quantify the amount of hydrogen present. Not only is hydrogen detection necessary for life safety reasons, but effective hydrogen monitoring is also required for optimal process control of hydrogen-based energy systems. These needs call for a sensor technology that can accommodate many diverse requirements. For industrial applications, sensors must be hydrogen-selective and immune to impurity gases commonly present in hydrogen feedstock. A fast speed of response is a critical requirement for life safety monitoring and a necessary feature for real-time control of processes that run on rapid duty cycles. We have developed and characterized novel Micro-Electro-Mechanical System (MEMS)-based hydrogen sensors to meet this growing need.

The novel hydrogen sensors developed at ATMI are based on a MEMS device platform. The MEMS platform, known as a micro-hotplate, is a suspended thermal isolation structure with an embedded heater element (Semancik, *et al.*, 2001). The new sensors employ rare earth metal thin films as the active sensing layer and use reversible metal hydrogenation as the sensing mechanism. The extent of hydrogenation depends on the gas-phase hydrogen concentration, and hydrogenation can increase the electrical resistance by several orders of magnitude, making it a very sensitive transduction mechanism.

Approach

Our approach has been to design, fabricate, and characterize MEMS-based gas sensors of different layouts and film chemistries. The understanding gained during characterization is subsequently used as feedback to the next design cycle. A schematic of the layered structure that makes up the sensor is shown in Figure 1. The micro-hotplate layout was designed in-house and fabricated by a foundry service. A rare earth metal thin film with a palladium-based capping layer was subsequently deposited onto the micro-hotplate platform and serves as the active sensing layer. Substantial effort has been devoted to mapping the fabrication process flow, which involves 11 steps and over 110 variables. Knowledge-based management (Schmidt, *et al.*,

1999) and other data-driven quality control protocols have been applied to identify the issues affecting sensor yield and uniformity.

While the sensor construction is relatively straightforward, the sensor characteristics can be quite complex due to strong coupling of chemical reactions, electrical probing, and mechanical movement. For example, hydrogen must first adsorb, dissociate, and diffuse through the cap layer. Upon reaching the sensing layer, it reacts with the sensing material to form hydride of relevant phases. When the hotplate temperature is raised above ambient to expedite these chemical reactions, it also modifies the hydrogen content and electrical resistance of the hydride film and causes the micro-hotplate platform to deflect. The deflection in turn modifies the stress state of the sensor stack, changing the film properties. We have used a wide variety of microscopy techniques as well as electrical characterization to study and model sensor behaviors.

Results

Using KBM techniques such as resistance as a function of H_2 concentration, temperature, and voltage, we identified the contact interface between the Al interconnect and the sensing layer as a primary candidate for improvement in order to improve yields and uniformity. It was further determined that the interface layer was affected by both non-planar surface topography and the formation of native oxide on the surface of the Al interconnect prior to deposition of the sensing layer. Process steps were

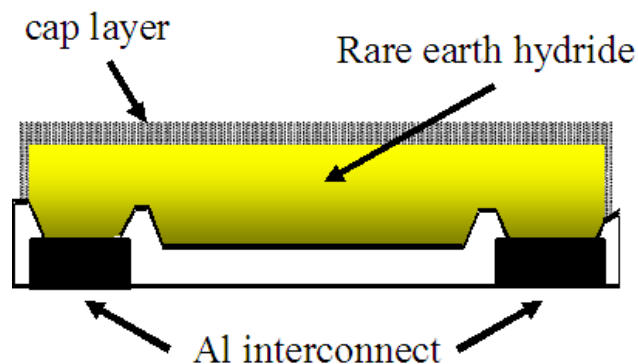


Figure 1. Schematic of Functional Layer Stack on a Micro-Hotplate Platform

added to planarize the structure and clean the contact area *in situ*. A representative result comparing the surface topography of a sensor structure, measured by stylus profilometry, before and after the planarization step is shown in Figure 2. The new processing steps help ensure that the sensing layer deposited is uniform across the platform surface, and that there is good electrical contact to the underlying Al interconnects. Addition of these steps to the fabrication process improved the pre-packaging yield to greater than 80% and reduced intra-die variation, as shown in Figure 3.

In addition to improving the fabrication yield, we have made appreciable progress towards understanding the chemical, electrical, and mechanical aspects of the sensing mechanism. The mechanical aspect had been less apparent in the past, but its effects are magnified now that additional processing steps have improved the electrical contact. Additionally, new microscopy techniques

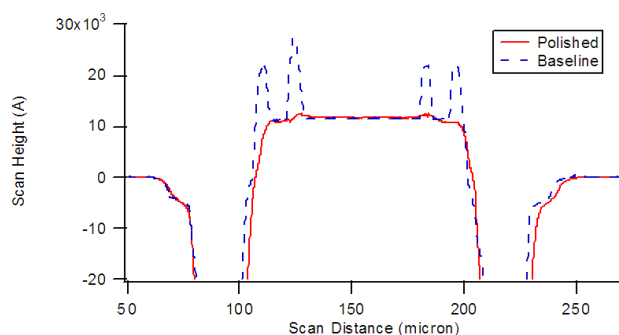


Figure 2. Representative Result of Surface Planarization

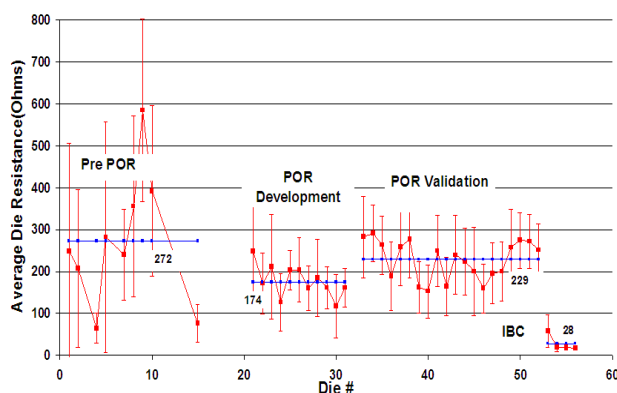


Figure 3. Yield Improvements as Function of Process Improvements vs. Process of Record (POR)

have enabled the visualization of the mechanical behavior for the first time. In particular, bending of micro-hotplate platform has been observed via a confocal microscope, as shown in Figure 4. Moreover, as the hydride film absorbs hydrogen, its volume expands, and the extent of deflection changes. The heater element embedded on the micro-hotplate platform, made of a piezo-resistive element, changes its electrical resistance when the deflection modifies the stress states of the platform. It was recognized that this phenomenon can serve as the basis for a separate, piezo-resistive mechanism in addition to the original chemi-resistive mechanism for signal transduction. Chemi- and piezo-resistive responses of a representative sensor are shown in Figure 5. The two mechanisms together, with no modification to sensor construction, provide a unique sensor package that has high sensitivity around lower explosion level (LEL - 4% H₂ in air) and a large dynamic range beyond LEL.

An electronic signal conditioning and processing system was developed to provide a simple device for collaborators to interface with their detection system. The system includes signal conditioning circuitry for proper power sourcing and resistance measurement, as well as real-time signal processing software running on a microprocessor embedded on the circuitry. When coupled with a data-logging device such as a personal digital assistant, as illustrated in

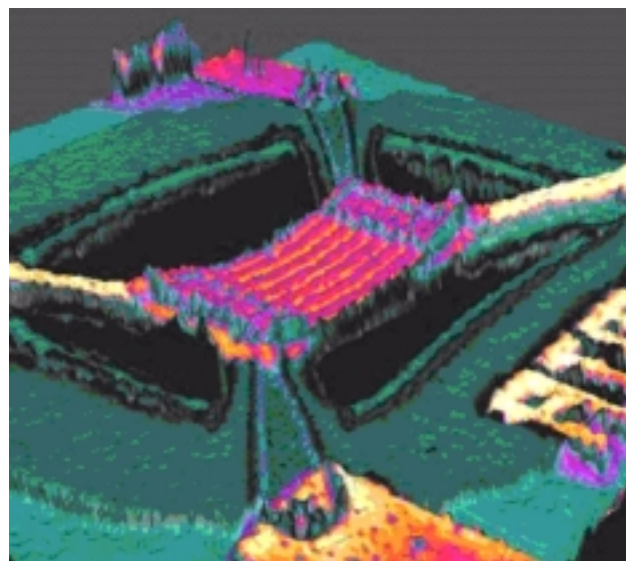


Figure 4. Representative Confocal Microscopy Image of a Sensor

Figure 6, the system becomes a stand-alone unit that can be easily transferred to test sites to verify sensor performance in real-life settings. Systems have been deployed at several locations in the U.S. and Europe.

Conclusions

- Improved fabrication yield and device uniformity have been demonstrated.
- The interdependency of chemical, electrical, and mechanical properties of the sensor operation has been characterized and studied.
- An innovative piezo-resistive transduction mechanism was discovered.
- Signal conditioning/processing of sensor response was implemented for system integration.

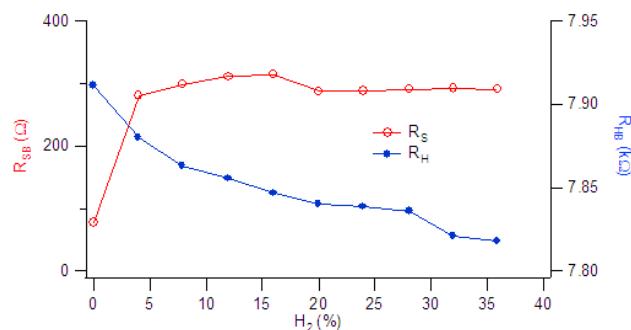


Figure 5. Representative Sensor Responses up to 40% H₂



Figure 6. Photo of an Evaluation Kit with Signal Conditioning/Processing Capability

- KBM techniques have been applied with encouraging feedback for the continuing improvement of sensor fabrication.

References

1. S. Semancik, R.E. Cavicchi, M.C. Wheeler, J.E. Tiffany, G.E. Poirier, R.M. Walton, J.S. Suehle, B. Panchapakesan, D.L. DeVoe, *Sensors and Actuators B* 77, 579 (2001).
2. S.R. Schmidt, M.J. Kiemele, and R.J. Berdine, *Knowledge Based Management*, Air Academy Press & Associates, CO, 1999.

FY 2003 Publications/Presentations

1. "MEMS based hydrogen gas sensors," submitted to *Journal of Electrochemical Society*.
2. "MEMS based hydrogen sensors for emerging applications," presented at *Connecticut Microelectronics and Optoelectronics Consortium Symposium*, Storrs, Connecticut (2003).

Special Recognitions & Awards/Patents Issued

1. G. Bhandari and T.H. Baum, "Hydrogen sensor utilizing rare earth metal thin film detection element," U.S. Patent 6,006,582 (1999)
2. F. DiMeo and G. Bhandari, "Micro-machined thin film hydrogen gas sensor, and method of making and using the same," U.S. Patent 6,265,222 (2001)
3. F. DiMeo and T.H. Baum, "Micro-machined thin film sensor arrays for the detection of H₂, NH₃, and sulfur containing gases, and method of making and using the same," U.S. patent application 2002/0017126, allowed
4. F. DiMeo and P. Chen, "Rare earth metal sensor," U.S. patent pending
5. I.-S. Chen and F. DiMeo, "Chemical sensor responsive to change in volume of material exposed to target particle," U.S. patent pending